

# Chemistry

## Lecture 2

By: Syed Ali Shan

### Hydrocarbons

#### Outline:

- ✚ Open chain and closed chain hydrocarbons
- ✚ Nomenclature of alkanes, alkenes and alkynes
- ✚ Benzene, properties, structure, modern representation, resonance method, Electrophilic substitution
- ✚ The molecular orbital treatment of benzene

#### Classification of Hydrocarbons

##### A) Open chain/Ayclic/Aliphatic

###### Saturated Hydrocarbons (Alkanes):

- Valencies of carbon atoms are fully satisfied
- They cannot take up any hydrogen atom or any other atom
- Generally give substitution reactions

###### Unsaturated Hydrocarbons (Alkenes):

- Valencies of carbon atoms are not fully satisfied
- They can take up any hydrogen atom or any other atom
- Generally give addition reactions

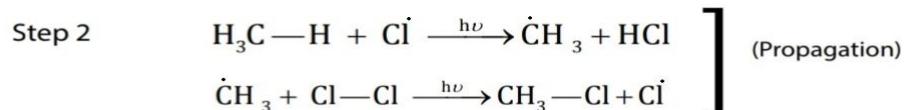
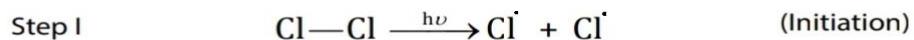
##### B) Closed chain/Cyclic Hydrocarbons $\Rightarrow$ Alicyclic and Aromatic (Discussed in previous lect.)

#### Alkanes

- General formula  $C_nH_{2n+2}$
- Paraffins
- Non polar, weak London forces
- Low M.P and B.P, increases with molecular mass or carbon chain
- $Sp^3$ -hybridization
- Least reactive among hydrocarbons due to:
  - ☞ Non polar nature of C-H and C-C bonds
  - ☞ Inertness of  $\sigma$  bond
- Give free radical substitution reactions and thermal/catalytic reactions.

## Halogenation

- ❖ Addition of halogen
- ❖ Free radical mechanism
- ❖ In presence of diffused sunlight
- ❖ 3 steps (initiation, propagation, termination)
- ❖ Reactivity order  $F_2 > Cl_2 > Br_2 > I_2$
- ❖  $F_2$  reacts violently
- ❖  $I_2$  reacts too slowly and reaction is reversible
- ❖ R-I is not produced
- ❖ Mixture of products are obtained
- ❖ In excess of methane,  $CH_3Cl$  is major product
- ❖ In excess of  $Cl_2$ ,  $CCl_4$  is major product



By repetition of step II, a mixture of halogen substituted products are obtained. The reaction is not synthetically so important.



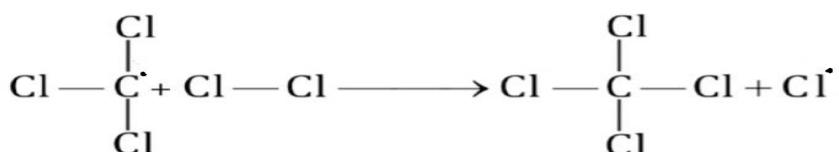
Dichloromethane



Chloroform



Tetrachloromethane or  
carbon tetrachloride



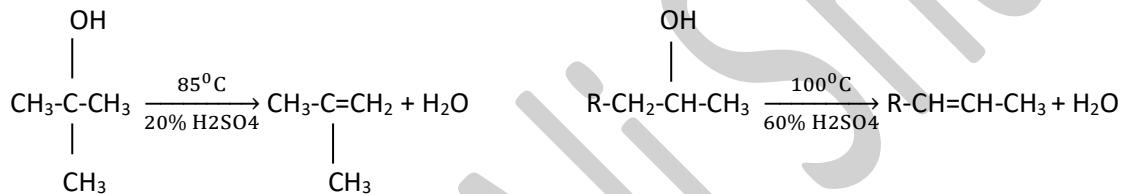
## Alkenes

- Olefins (oil forming property)
- General formula  $C_nH_{2n}$  (for mono-enes)
- Each double bonded carbon is  $sp^2$  hybridization
- Ethene ( $CH_2=CH_2$ )  
The simplest alkene  
Has 5 sigma (4 with hydrogen atoms and 1 b/w both carbons) and 1 pi bond (b/w both carbons)  
Has localized pi electrons

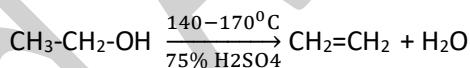
## Preparation of Alkenes

### (a) Dehydration of Alcohols:

$3^0$  alcohols  $> 2^0$  alcohols  $> 1^0$  alcohols (due to stability of carbocation, an intermediate)



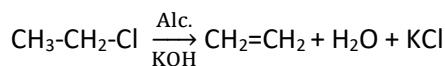
(In case of possibility of more than one kind of alkene products, choose the symmetrical alkene as product)



- What will be the product of dehydration of 2-Pentanol?
- ◆ **Dehydrating agents:**  $\text{Al}_2\text{O}_3$ (best method),  $\text{P}_4\text{O}_{10}$  or  $\text{P}_2\text{O}_5$ , conc. $\text{H}_2\text{SO}_4$ ,  $\text{H}_3\text{PO}_4$

### **(b) Dehydrohalogenation of Alkyl Halides:**

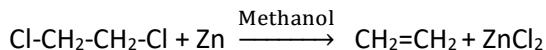
- $\beta$  elimination reactions (E reactions)
- $\beta$  hydrogen is removed along with halogen
- Occurs in presence of **Alcoholic KOH**
- Product is alkene
- Primary alkyl halides give E2
- Tertiary alkyl halides give E1
- Secondary alkyl halides give both E2 and E1
- If more than one  $\beta$  hydrogen are present then  $\beta$  hydrogen will be removed as so to form **symmetrical alkene**.



- What will be the product of dehydrohalogenation of 2-Chloro butane?

**(c) Dehalogenation of Vicinal dihalides:**

- Reaction with active metals like Mg, Zn dust (reduction) etc
- In anhydrous solvent i.e. methanol ( $\text{CH}_3\text{OH}$ ) or acetic acid



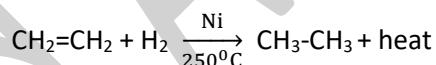
### Reactions of Alkenes

- Mostly give electrophilic addition reactions
- Most reactive hydrocarbon
- Due to pi bond formed by sideways overlap (less overlap)
- Weaker than sigma bond

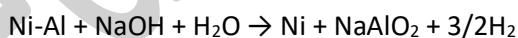
**(a) Addition Reactions:**

**i. Hydrogenation (Reduction):**

- Catalyst  $\gg \text{Ni}/250^\circ\text{C}$  or  $\text{Pt}, \text{Pd}/\text{room T}$
- Amount of heat evolved is called heat of hydrogenation
- Used in quantitative analysis
- Used in preparing vegetable ghee from vegetable oil
- Used as Synthetic as well as analytical tool



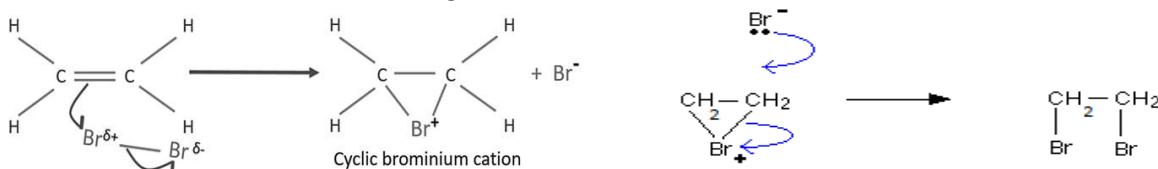
**Raney Nickel**



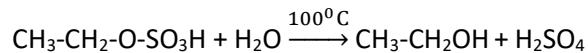
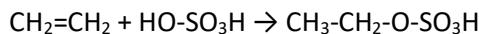
- Raney nickel has porous surface (high surface area)

**ii. Halogenation:**

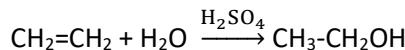
- $\text{F}_2 > \text{Cl}_2 > \text{Br}_2 > \text{I}_2$
- Bromine water test
- Unsaturation test
- $\text{Br}_2/\text{CCl}_4$  is added
- Brown colour of bromine discharges



### iii. Hydration:



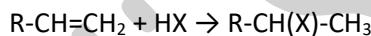
OR



- OH group will attach with that double bonded carbon which has less no. of hydrogen atoms
- Which alkenes produce 2-Butanol?

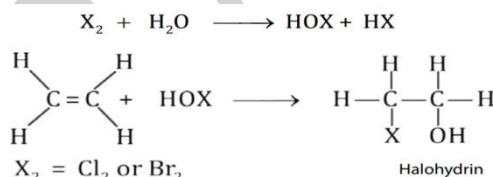
### iv. Addition of Hydrogen Halides/Halogen Acids:

**Markownikov's Rule:** On addition of unsymmetrical reagent to unsymmetrical alkene/alkyne, negative part of the adding reagent goes to that double bonded carbon having less no. of hydrogen atoms and positive part to that double/triple bonded carbon having more hydrogen atoms.



- Reactivity order **HI > HBr > HCl > HF**
- Two steps involved
- Alkene molecule acts as nucleophilic centre
- Intermediate formed during mechanism acts as electrophile

### v. Addition of Hypohalous Acid:

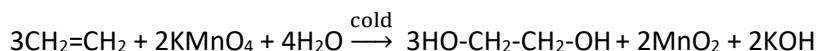


- OH is negative end and X is positive end of hypohalous acid

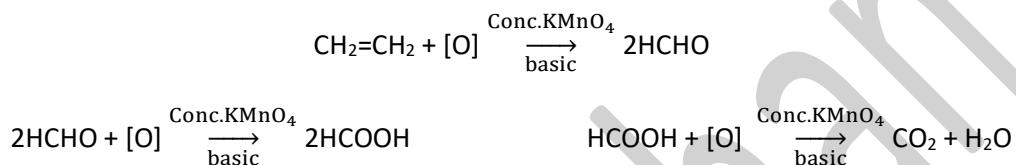
## (b) Oxidation Reactions:

### i. Hydroxylation:

- ◆ Dil. Cold  $\text{KMnO}_4$
- Unsaturation test
- Baeyer's reagent (cold 1% alkaline  $\text{KMnO}_4$  solution)
- Pink colour of  $\text{KMnO}_4$  discharges
- Products are stable vicinal glycols (simply glycols)
- These glycol can be oxidized to aldehydes and carboxylic acids by using strong oxidizing agents (conditional)



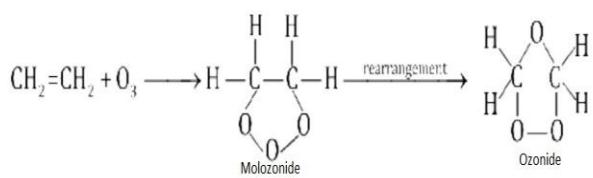
- The product ethylene glycol is stable under these conditions
- In presence of strong oxidizing agent, ethylene glycol will oxidize to form glyoxal which will further oxidize to oxalic acid
- ◆ **Conc. Hot KMnO<sub>4</sub>**
- Produces two molecules of carboxylic acid (final product if aldehyde was initially produced)
- Formic acid further oxidizes to CO<sub>2</sub>
- It is oxidative cleavage
- Unsaturation test as well as for the location of double bond
- Double bonded carbon will convert into carbonyl group



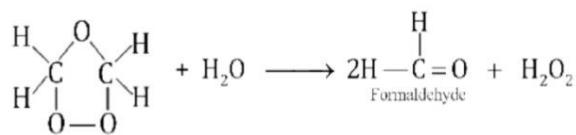
- Which alkene produces 1 mole of acetic acid and 1 mole of propanoic acid?

## ii. Ozonolysis:

- A test for location of double bond
- Ozone is allotropic form of oxygen
- Products are aldehydes/ketones



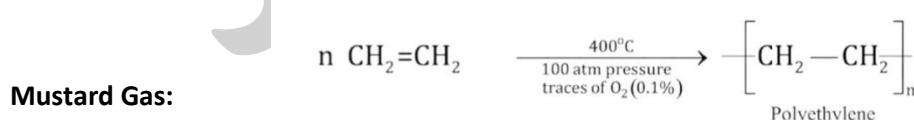
Ozonides are unstable compounds and are reduced directly by treatment with zinc and  $\text{H}_2\text{O}$ . The reduction produces carbonyl compounds (aldehydes or ketones).



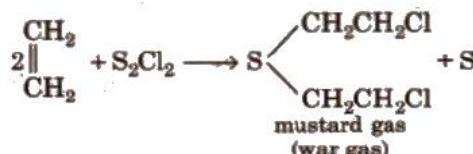
- 2-Butene will produce?

### (c) Polymerization:

- Small molecules combine to form large molecule
- C-C bond length is high in polymer than in monomer
- Mixture of  $\text{Al}(\text{C}_2\text{H}_5)_3$  and  $\text{TiCl}_4$  is used for good quality
- Optimum conditions; **T=400°C, P=100 atm, 0.1% O<sub>2</sub>, Catalyst [TiCl<sub>4</sub> + Al(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>]**



## Mustard Gas:



- High boiling liquid
- Highly vesicant
- Causes blisters

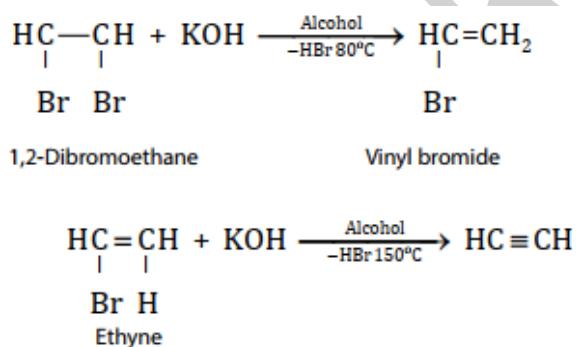
## Alkynes

- General formula  $C_nH_{2n-2}$  (for mono-ynes)
- Each triple bonded carbon is sp hybridization
- Ethyne ( $CH \equiv CH$ ), the simplest alkyne

## Preparation of Alkynes

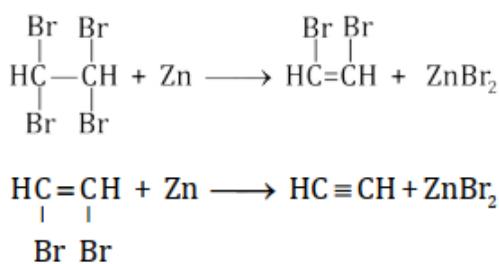
### (a) Dehydrohalogenation of Vicinal dihalides:

- $\beta$  elimination reactions (E reactions)
- $\beta$  hydrogen is removed along with halogen
- Occurs in presence of **Alcoholic KOH**
- Elimination occurs from adjacent carbons twice



### (b) Dehalogenation of Vicinal tetrahalides:

- Reaction with active metals like Mg, Zn dust (reduction) etc
- In anhydrous solvent i.e. methanol ( $CH_3OH$ ) or acetic acid

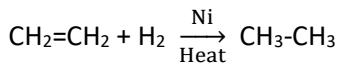
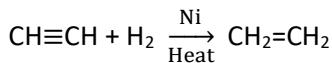


## Reactions of Alkynes

- Mostly give electrophilic addition reactions
- Less reactive than alkene towards electrophilic addition reaction due to presence of triple bond which reduces bond length making it difficult to break
- More reactive than alkene towards nucleophilic reagents

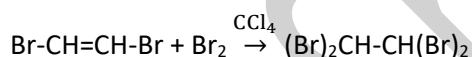
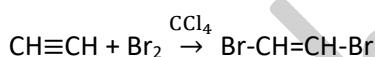
### (a) Addition Reactions:

#### i. Hydrogenation (Reduction):



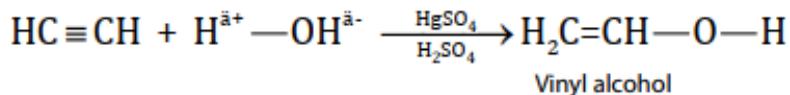
#### ii. Halogenation (addition of $\text{X}_2$ ):

- $\text{F}_2 > \text{Cl}_2 > \text{Br}_2 > \text{I}_2$
- Bromine water ( $\text{Br}_2/\text{CCl}_4$ ) test (unsaturation test)
- Brown colour of bromine discharges

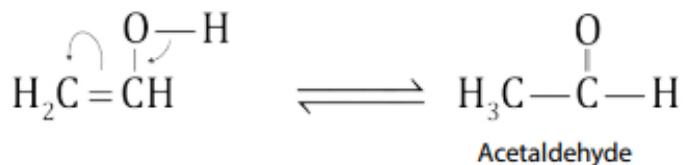


#### iii. Hydration (addition of $\text{H}_2\text{O}$ ):

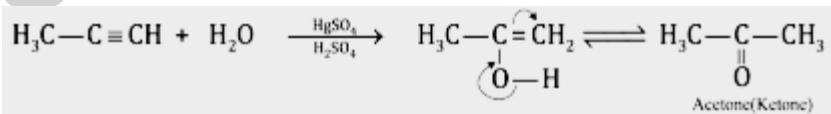
Water adds to alkynes in the presence of mercuric sulphate dissolved in sulphuric acid at  $75^\circ\text{C}$ . The reaction is important industrially. For example,



Vinyl alcohol is an unstable enol. The enol has the hydroxy group attached to a doubly bonded carbon atom and isomerises to acetaldehyde.



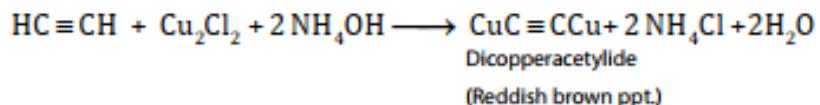
All other alkynes give ketones.



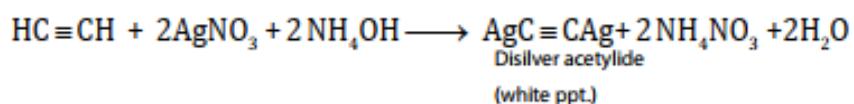
- Double bonded carbon to which  $-\text{OH}$  will be attached in enol form will become carbonyl group after rearranging.
- Butanone is produced from which alkyne?
- 2-pentyne produces .....ketone?

## Acidity of Alkynes

- ❖ Ethyne and terminal alkynes (1-alkynes) like propyne, 1-butyne, 1-pentyne show acidic nature
- ❖ Hydrogen is bonded to sp-hybridized carbon through sp-s overlap
- ❖ sp-hybridization makes carbon more electronegative
- ❖ sp-hybridized carbon pulls electrons towards itself making hydrogen atom acidic
- ❖ 1-Alkynes or ethyne form alkynides or acetylide [both ionic in nature] with molten Na and sodamide ( $\text{NaNH}_2$ )
- ❖ **Ammoniacal solution of cuprous chloride**



- ❖ **Ammoniacal solution of silver nitrate**



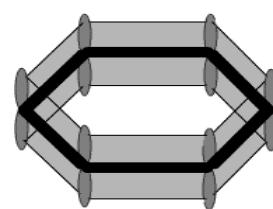
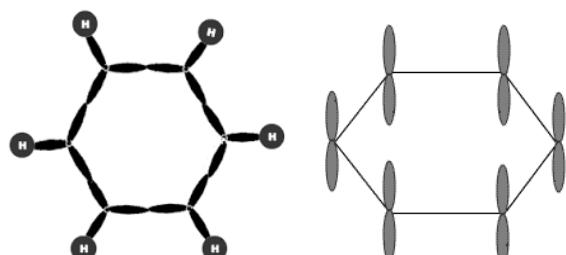
- ❖ Acetylide react with mineral acids i.e.  $\text{HCl}$ ,  $\text{HNO}_3$ ,  $\text{H}_2\text{SO}_4$  etc to recover acetylene
- ❖ These alkynides are used for the preparation, purification, separation, and identification of alkynes.

## Benzene

- Discovered by Michael Faraday by destructive distillation of vegetable oil.
- Found in coal-tar by Hoffmann.
- Benzene is a colorless liquid with particular smell and taste
- It is flammable

### Structure:

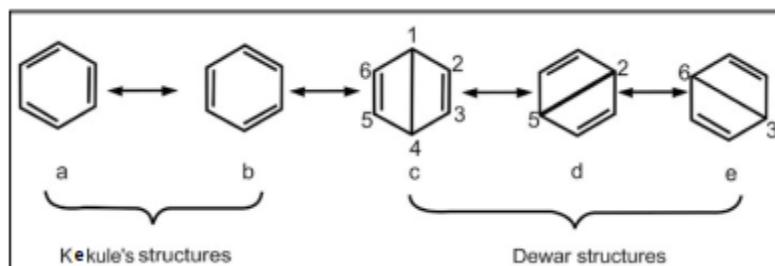
- Stability is explained on basis of;
  - Resonance method (resonance energy of benzene =  $+150.5 \text{ kJmol}^{-1}$ )
  - **Atomic orbital treatment**
- Each carbon is  $\text{sp}^2$  hybridized
- Hexagonal planner
- $120^\circ$  bond angle
- Delocalized pi electrons
- Stable molecule
- Continuous sheath of electronic cloud formed
- Sandwich structure obtained
- Strong electrophile is prepared
- Reluctant to electrophilic addition reactions
- Prefer electrophilic substitution reactions
- Don't give elimination and polymerization reaction



Continuous sheath of es-1

## Resonance method

- The possibility of different pairing scheme of valence electrons of atoms is called resonance and the structures thus obtained are resonance structures.



- Resonance hybrid structure is represented with circle (solid or dotted) inside the ring

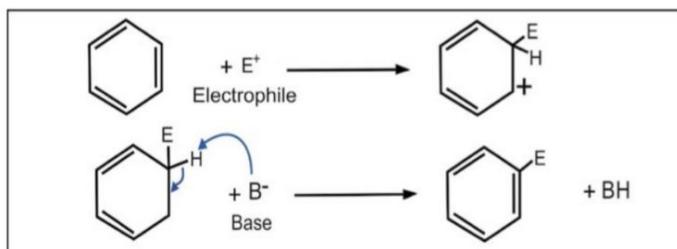


In alkanes the C-C bond length is 1.54 $\text{\AA}$ .  
In alkenes the C = C bond length is 1.34 $\text{\AA}$ .  
In alkynes the C ≡ C bond length is 1.20 $\text{\AA}$ .  
In benzene the C-C bond length is 1.397 $\text{\AA}$ .

## Electrophilic Substitution Reactions

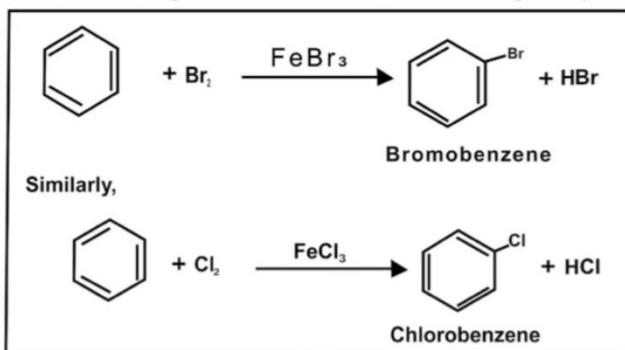
- These reactions prove benzene is very stable molecule
- Strong electrophile is required to break stable pi electronic cloud of benzene

### General Mechanism:



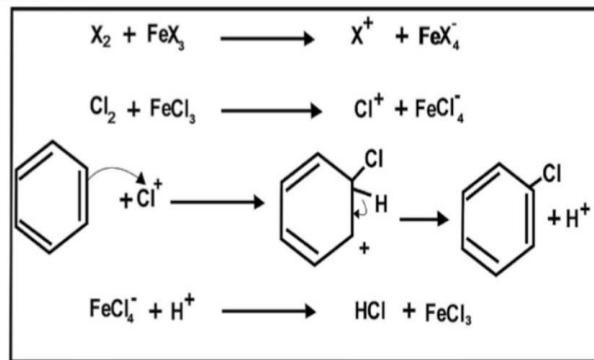
## 1. Halogenation

The introduction of halogen group in benzene ring is called "Halogenation". Benzene reacts with halogen in the presence of a catalyst like  $\text{FeBr}_3$ ,  $\text{AlCl}_3$ , etc. Chlorination and bromination are normal reactions but fluorination is too vigorous to control. Iodination gives poor yield.



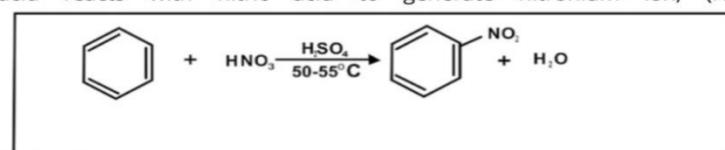
### Mechanism:

The actual halogenating agent is  $\text{X}^+$  (i.e.  $\text{Cl}^+$  or  $\text{Br}^+$ ) is formed by the following mechanism.

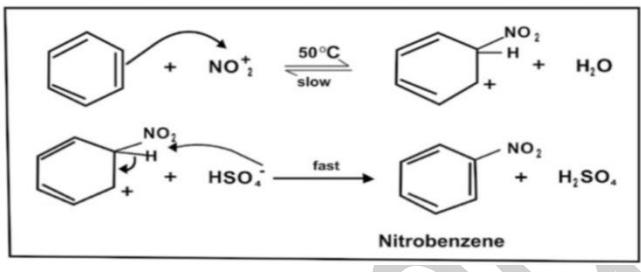


## 2. Nitration

The introduction of  $\text{NO}_2$  group in benzene ring is called "Nitration". The nitration of benzene takes place when it is heated with a 1:1 mixture of con.  $\text{HNO}_3$  and con.  $\text{H}_2\text{SO}_4$  at 50- 55°C. Sulphuric acid reacts with nitric acid to generate nitronium ion,  $(\text{NO}_2^+)$ .



### Mechanism:

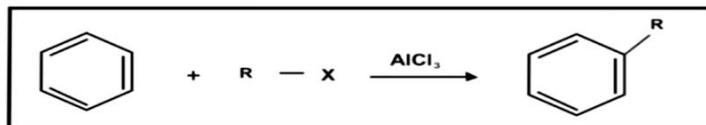


## 4. Friedel-Crafts Reactions

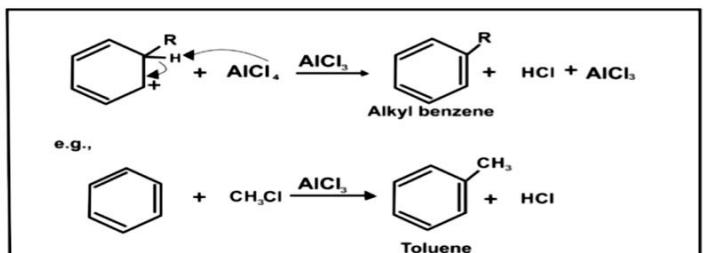
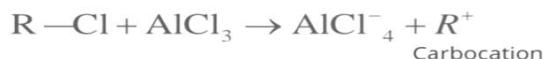
The alkylation and acylation of benzene are called Friedel-Crafts reactions.

### a) Alkylation

The introduction of an alkyl group in the benzene ring in the presence of an alkyl halide and a catalyst  $\text{AlCl}_3$  is called Friedel-Crafts alkylation or Alkylation.

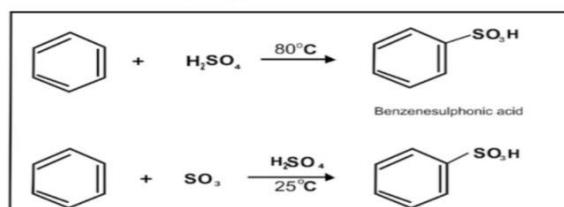


### Mechanism:



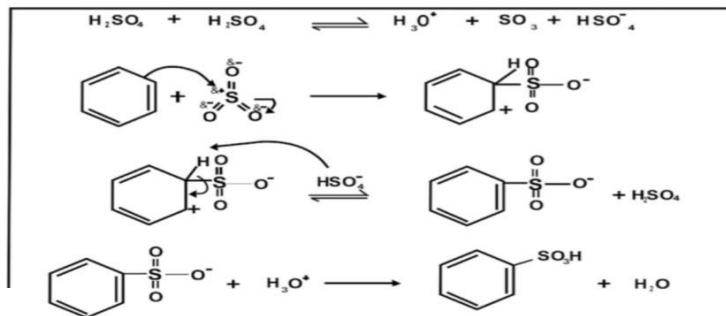
### 3. Sulphonation

The introduction of sulphonic acid group in benzene ring is called Sulphonation. When benzene is heated with fuming  $\text{H}_2\text{SO}_4$  or conc.  $\text{H}_2\text{SO}_4$  it yields benzene sulphonic acid.



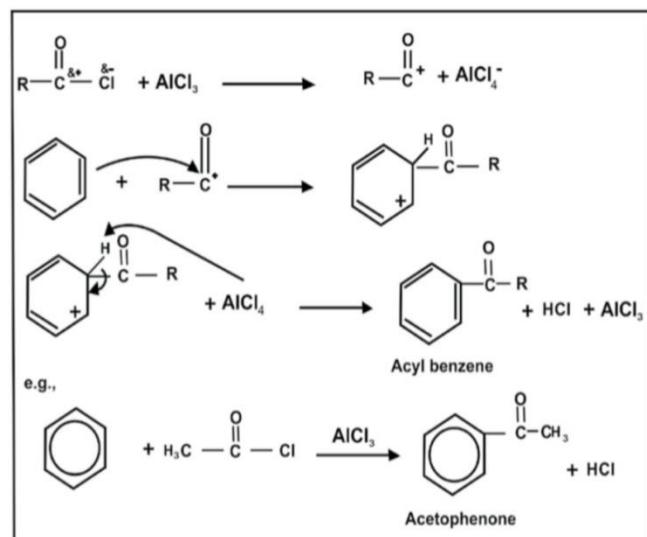
### Mechanism:

When sulphuric acid alone is used, the actual electrophile in this reaction is  $\text{SO}_3^+$ .



### b) Acylation:

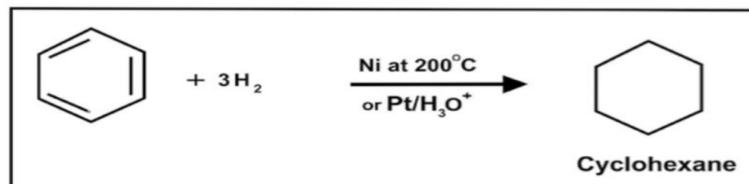
The introduction of an acyl group  $\text{R}-\overset{\text{O}}{\parallel}\text{C}-$  in the benzene ring in the presence of an acyl halide and a catalyst  $\text{AlCl}_3$  is called Friedel Crafts Acylation or Acylation.



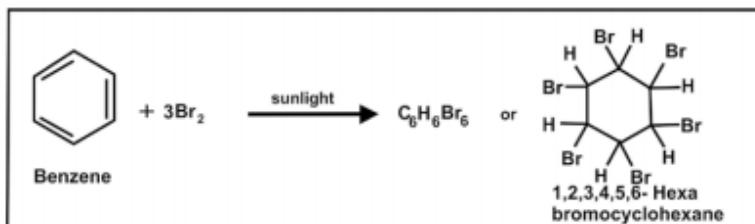
- Positive electrophiles in Electrophilic substitution reactions are called as .....onium ions i.e.  $\text{Cl}^+$  chloronium ion,  $\text{NO}_2^+$  nitronium ion,  $\text{R}^+$  alkyl cation ion,  $\text{CH}_3^+$  methyl cation ion,  $\text{RCO}^+$  acylium ion,  $\text{CH}_3\text{CO}^+$  acetyl cation ion etc.
- Introduction of  $\text{CH}_3^+$  in benzene ring is called Methylation
- Introduction of  $\text{HCO}^+$  is called Formylation and  $\text{CH}_3\text{CO}^+$  Acetylation
- In all Electrophilic substitution reactions hybridization changes from  $\text{sp}^2$  (planar) in benzene to  $\text{sp}^3$  (tetrahedral) in intermediate and finally to  $\text{sp}^2$  (planar) in product.

### Addition Reactions

#### Hydrogenation of Benzene



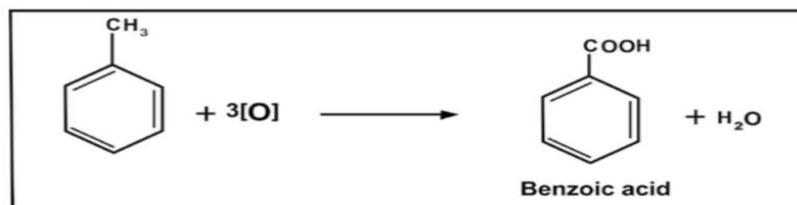
#### Halogenation of Benzene



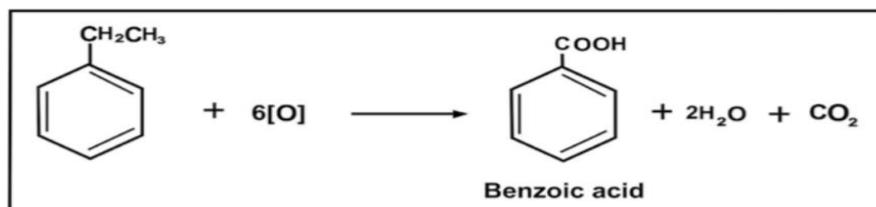
### Side chain Reactions

#### Side chain Oxidation of Benzene (alkyl benzene)

- Strong oxidizing agent ( $\text{KMnO}_4/\text{H}_2\text{SO}_4$ ) is used
- Pink colour of  $\text{KMnO}_4$  discharges
- Distinguish alkyl benzenes from other substituted benzenes

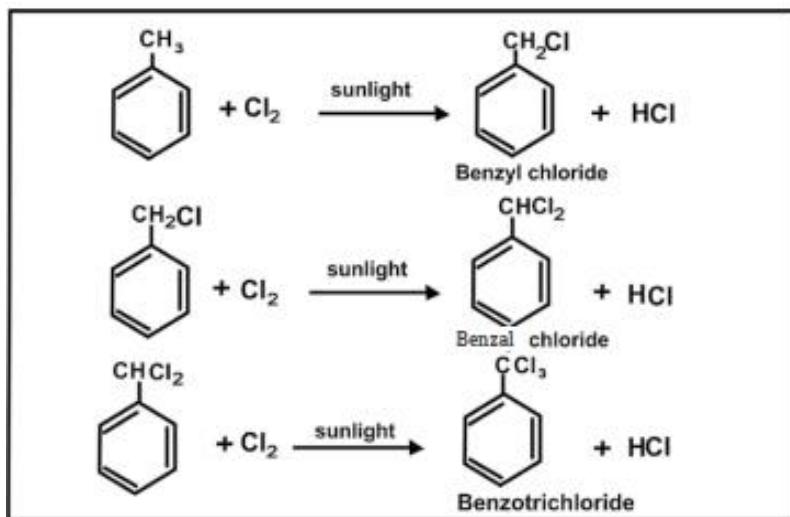


Whatever the length of an alkyl group may be it gives only one carboxyl group. Moreover the colour of  $\text{KMnO}_4$  is discharged. Therefore this reaction is used as a test for alkylbenzenes.



- Benzoic acid is the product

### Side chain Halogenation of Benzene (Methyl benzene)



### Substitution on Benzene Ring by 2,4- directing or 3,5- directing Groups

2,4 (Ortho-para directing groups)	3,5 (meta directing groups)
Electron donating	Electron withdrawing
Release electron on benzene ring	Withdraw electron from benzene ring
Increase availability of electrons on 2,4 positions	Decrease availability of electrons on 2,4 positions
Direct the attack of electrophile at 2, 4 positions	Direct the attack of electrophile at 3, 5 positions
Activate the ring (except halogens)	Deactivate the ring (decrease nucleophilicity of benzene)
Increase nucleophilicity of benzene	
Ex.: -CH <sub>3</sub> , -NH <sub>2</sub> , -NHR, -SH, -OCOR, -OH, -OCH <sub>3</sub> , -N(CH <sub>3</sub> ) <sub>2</sub> , -Cl, -Br, -I	Ex.: -NO <sub>2</sub> , -NR <sub>3</sub> <sup>+</sup> , -CN, -COOH, -CHO, -COR, CCl <sub>3</sub>